Study on some factors affecting the process of synthetic MIL-100(Fe) by sonochemical synthesis method

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ABSTRACT

The Metal-Organic Framework material MIL-100(Fe) has been synthesized into iron (III) based on a 1,3,5 benzentricacboxylic organic ligand (H_3BTC) by sonochemical synthesis method using a solvent that is water. Factors that affect the synthesis of materials have been investigated including sonochemical synthesis power, reaction time, reaction rate and reactant concentration. Research results show that the suitable condition for the synthesis of MIL-100 (Fe) materials by the sonochemical method is the Fe^{3+}:H_3BTC=3:2 reaction ratio with sonochemical synthesis power of 1080 W at a concentration of 0.1 M for a period of 10 minutes for a reaction yield of more than 72%. The resulting material was subjected to X-ray diffraction analysis, and surface area BET. The synthesized material has a high surface area of up to 1033.8 m^2/g and a pore volume of 0,79 cm^3/g.

Keywords: MIL-100(Fe); Sonochemical synthesis method; Reaction yield.

1. INTRODUCTION

In recent years, Metal-Organic Framework materials (MOFs) have attracted attention from researchers due to their high surface area, small particle size and some of their characteristic chemical properties (MOFs) [1, 2]. MOFs can be used in many potential applications such as storage and air separation, environmental treatment, etc. [3-5].

As a transition metal, iron (III) ions are very popular and used as a metal center for metal frame structures. Iron (III) -based organometallic framework materials are often synthesized together with organic ligands such as terephthalic acid [6, 7], 1,3,5 benzentricacboxylic [8, 9] or 2-aminoterephthalic acid [10]. The Metal-Organic Framework material has been synthesized into iron (III) based on organic ligand has many applications in different. In addition, with biocompatibility properties, iron-based Metal-Organic Framework materials are also promising applications in the field of drug absorption [4, 11].

MOFs based on iron can be synthesized by many different methods such as hydrothermal, reflux, microwave and sonochemical [5, 7, 9], etc. In particular, the sonochemical method is a very simple method with a fast synthesis time, ideal yield and less energy consumption. Besides the use of green solvents such as water, ethanol, etc. this is a possible method towards green chemistry [12].

The process of synthesizing materials by sonochemical method depends on factors such as reaction rate, reaction concentration, reaction power, reaction time, etc. In this study, we investigate the influence of the above factors on the synthesis of materials by sonochemical method.

2. EXPERIMENT

2.1. Chemicals, equipment

Chemicals: Iron(III)chloride $FeCl_3.6H_2O$; 1,3,5 benzentricacboxylic acid (1,3,5 BTC) and ethanol (C_2H_5OH) were purchased from Macklin, distilled water.

Equipment: Sonochemical machine, centrifuge, drying cabinet.

2.2. Synthesis of materials

2.2.1. Surveying the effect of the reactant ratio

The experimental samples were fixed with a mass of 2.8 g H_3BTC and a mass change of $FeCl_3.6H_2O$ according to the respective molar ratios of 1:2; 2:3; 1:1; 3:2; 2:1 in 200 mL of distilled water. Then, the samples were then transducer ultrasound for 10 minutes with a power of 1800 W, a frequency of 20.5 kHz. The material obtained after the reaction was filtered and washed 3 times with ethanol and distilled water, and then dried at 100 ^oC.

2.2.2. Surveying the effect of sonochemical power

The experimental samples were fixed with a molar ratio of 3:2 between $FeCl_3$: H_3BTC wtith a concentration of 0.1 M in 200 ml distilled water, the reaction was carried out at different powers: 360 W, 720 W, 1080 W, 1440 W, 1800 W. Then, the samples were transducer ultrasound for 10 minutes, a frequency of 20,5 kHz. The material obtained after the reaction was filtered and washed 3 times with ethanol and distilled water, and then dried at 100 ^oC.

2.2.3. Surveying the effect of reactant concentration

The experimental samples were fixed with a molar ratio of 3:2 between $FeCl_3$: H_3BTC and changed the mass of reactants according to the concentrations in the respective solution 0.125 M; 0.1 M; 0.075 M; 0.05 M; 0.025 M in 200 ml distilled water. Then, the samples were then transducer ultrasound for 10 minutes with a power of 1080 W, a frequency of 20.5 kHz. The material obtained after the reaction was filtered and washed 3 times with ethanol and distilled water, and then dried at 100 ^oC.

2.2.4. Surveying the effect of reaction time

The experimental samples were fixed with a molar ratio of 3:2 between $FeCl_3$: H_3BTC with a concentration of 0.1 M in 200 ml distilled water, the reaction was carried out at different synthesis times: 2 minutes, 4 minutes, 6 minutes, 8 minutes and 10 minutes. Then, the samples were then transducer ultrasound above periods with a power of 1080 W, a frequency of 20.5 kHz. The material obtained after the reaction was filtered and washed 3 times with ethanol and distilled water, and then dried at 100 ^oC.

2.3. Characteristic evaluation of material properties

The synthesized materials were evaluated for structure by X-ray diffraction at Hanoi University of Science and Technology, infrared absorption spectroscopy (FT-IR) analysis method at Institute of Chemistry - Materials. The morphology of the material was measuring the BET surface area at the Institute of Materials Science, Vietnam Academy of Science and Technology.

The reaction percentage yield is expressed as:

$$H = \frac{m_{ex}}{m_{th}} .100\%$$

Where: H is percentade yield, %;
m_{ex} : Weight of product;
m_{th} : Theoretical yield.

3. RESULT AND DISCUSSION

3.1. Effect of reactant ratio

The synthesized material is yellow-brown, fine powder (figure 1). The crystals of the material were surveyed by X-ray diffraction. The results showed that the material had characteristic peaks at 11^o, 19^o, 24^o, 28^o similar to the standard spectrum. The low peak height and obtuse peak are due to the material synthesized by the sonochemical method with low-

pressure conditions and fast reaction time, limiting the crystal growth of the material. Besides, the synthetic solvent is water, so the material is formed right on the insoluble organic acid crystals (heterologous reactions), which is different from the material formed from homo-crystallization, so the crystallinity of the material is not high (figure 2). The results obtained were similar to other samples obtained in synthesis conditions such as changes in power, time reaction and reaction concentration.

Figure 1. *Material after drying.*

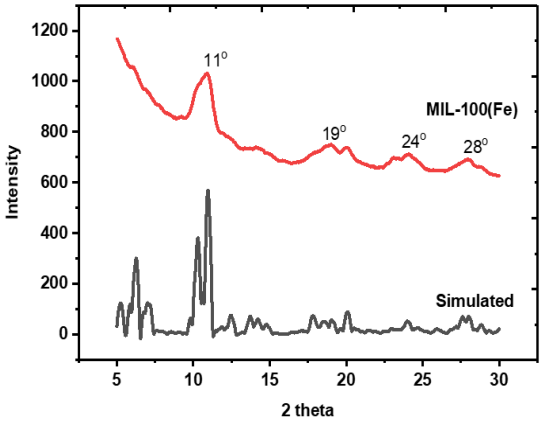

Figure 2. *X-ray diffraction spectrum.*

The results of comparing the mass of the product obtained when fixing the amount of acid participating showed that the product obtained gradually increased when increasing the reaction ratio between $FeCl_3$ and H_3BTC from 1:2 to 3:2 and peaking at a ratio of 3:2 (table 1).

Table 1. *The table compares the mass of products obtained from different reaction ratios.*

The ration ($FeCl_3$:H_3BTC)	**Mass of H_3BTC (g)**	**Mass of $FeCl_3.6H_2O$ (g)**	**Mass of FeBTC (g)**
1:2	2,8	1,8	0,882
2:3	2,8	2,4	2,043
1:1	2,8	3,6	2,656
3:2	2,8	5,4	3,238
2:1	2,8	7,2	3,034

Then, after increasing the amount of $FeCl_3$, the volume of the product does not increase. This result is also consistent with reaction equation (1) proposed below with a molar ratio of iron and acid is 3:2.

$$3FeCl_3.6H_2O + 2H_3BTC + H_2O \rightarrow Fe_3O(H_2O)_2(OH)BTC_2 \quad (1)$$

3.2. Effect of sonochemical power

The reaction yield of material synthesis at different powers with the same reaction time is shown in figure 3. The results of the reaction yield showed that the power did not have much influence on the reaction yield. At 360 W, the reaction yield reached 55.21%. From 720 W to 1800 W, the reaction yields gradually increased from 61.13% to 74.61 %. When reacting at power 1800 W, the reaction yield reached 74.61% and was unchanged compared to the yield at 1080 W and 1440 W reached over 72%. Besides that, the power consumption is higher, so the

reaction can be performed at 1080 W to 1440 W to ensure yield, save reactive energy and be safe for equipment operation.

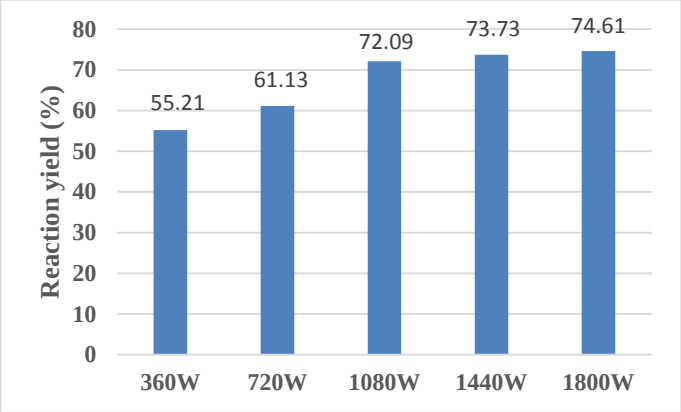

Figure 3. *Comparison chart of reaction yields at different powers.*

The porous properties of the material were investigated by N_2 gas adsorption isotherm. The adsorption isotherms of the material samples are of type II (according to IUPAC classification), showing that the material has a medium capillary form (figure 4). The results show that the surface area will be changed at each different power of pore volume. Power at 360 W lowest surface area (192 m^2/g according to BET), increasing power to 720 W, surface area according to BET also increases, continues to increase power up to 1080 W and at 1440 W results in according to BET reached high values 1033 m^2/g and 1080 m^2/g, when increasing the power to the value of 1800 W, the results according to BET decreased slightly, reaching 757 m^2/g (table 2).

Table 2. *Comparison table of porous properties of material at different powers.*

Synthesis power	Surface Area in BET (m^2/g)
360 W	192.17
720 W	368.0
1080 W	1033.78
1440 W	1040.11
1800 W	757.47

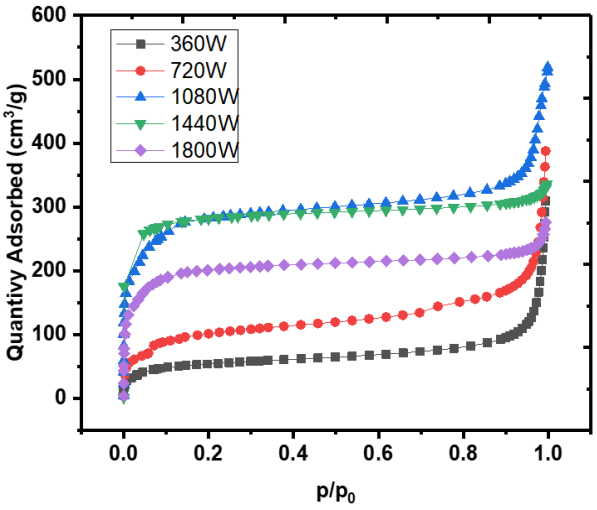

Figure 4. *N_2 gas adsorption isotherm of material at different powers.*

When the energy is low, the crystal formation process takes place slower, so there are incomplete crystals, the residual acid also affects the specific area of the surface of the material. But when the energy is too large, it is also a factor that causes the bonds to break, leading to a decrease in the specific surface area of the material. Thus, through the survey process, it is possible to choose the optimal synthesis conditions for MIL-100(Fe) materials with high surface area (1033 m^2/g) and reaction yield (72%) while ensuring the energy saving factor is at power 1080 W.

3.3. Effect of reactant concentration

As shown in figure 5, at low reactant concentrations of 0.025M; 0.05M the reaction yield is only from 37% to 49%. This can be explained because when the reactant concentration is lower, the possibility of acid contact with iron salts (especially since this is a heterogeneous reaction between insoluble acids and soluble iron salts) leads to lower reaction rates. As the reaction concentration increases, the reaction process is faster. But the higher the reaction concentration, the more time it takes for the reaction to increase, so to fix the reaction time of 10 minutes, the efficiency of the 0.125 M sample tends to decrease slightly. Therefore, with a fixed power of 1080 W and a time of 10 minutes, the appropriate concentration for the reaction to achieve the highest yield is from 0.075M to 0.1 M.

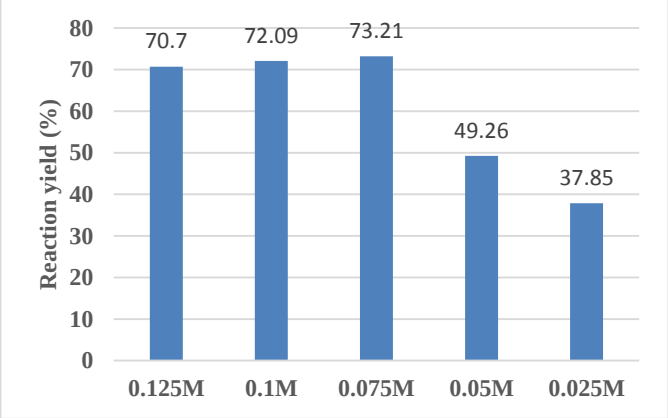

Figure 5. *Comparison chart of reaction yields at different concentrations.*

The porosity of the material samples at different reaction concentrations was surveyed by the N_2 gas adsorption isotherm (figure 6). The results showed that the surface area of the material gradually increased as the concentration of reactants increased from 0.025 M to 0.075 M, respectively, from 439 m^2/g to 1080 m^2/g.

Table 3. *Table comparing specific surface areas of samples at different concentrations.*

Reactant concentration (M)	Surface Area in BET (m^2/g)
0.025	439
0.05	559
0.075	1080
0.1	1033
0.125	1017

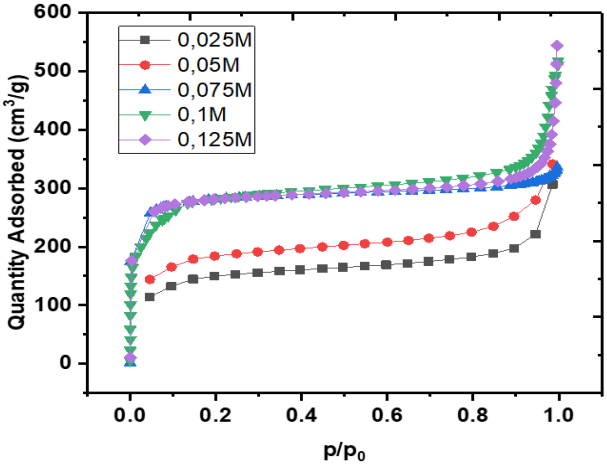

Figure 6. *N_2 gas adsorption isotherm of material at different concentrations.*

This can be explained, when at lower concentrations, the rate of aggregation and growth of the material crystals is low, leading to the porous structure of the incomplete material (with a short reaction time), so the porous nature of the material is very low. When continuing to increase the corresponding reaction concentration in the range of 0.075 M to 0.125 M, the

specific surface area is unchanged (from 1017 m^2/g to 1080 m^2/g), which shows that at this concentration range, the formation and structure development of the material is equivalent.

3.4. Effect of the reaction time

The results of the reaction yield showed that at the reaction time of 2 minutes, the reaction yield was low by 19.24%. It is possible that due to the short reaction time, the energy provided for the crystal formation reaction is not enough, so the obtained yield is not high. After 6 minutes, 8 minutes, 10 minutes and 20 minutes of reaction, the yield has increased rapidly to more than 72%, similar to some other claims that the process of forming crystals of the material is the same as the polymerization process, it takes enough time for the material to form a frame structure, so at short synthesis time the yield is low.

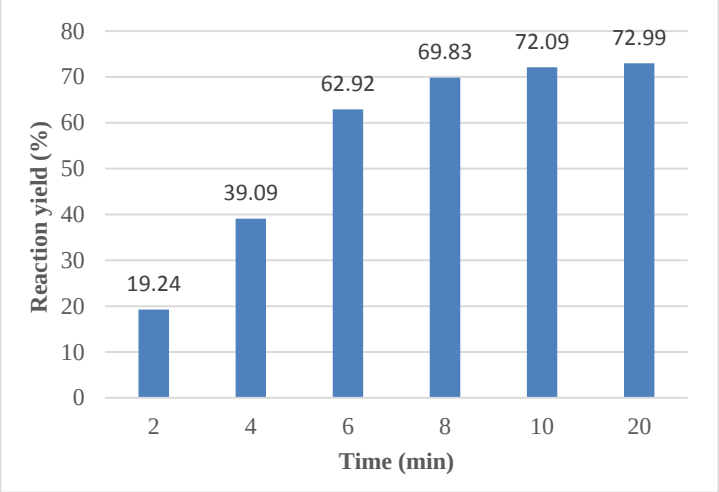

Figure 7. *Variation of reaction yields with reaction time.*

Reaction time from 10 minutes to 20 minutes, the reaction yield was unchanged significantly. Therefore, it is possible to choose the time to synthesize MIL-100(Fe) materials from 8 minutes to 10 minutes to both ensure the reaction yield and save time.

Table 4. *Surface area in BET of FeBTC materials at different synthesis times.*

Synthesis time (minutes)	Surface Area in BET (m^2/g)
2	81.6
4	146.4
6	367.2
8	887.8
10	1033.8
20	939.8

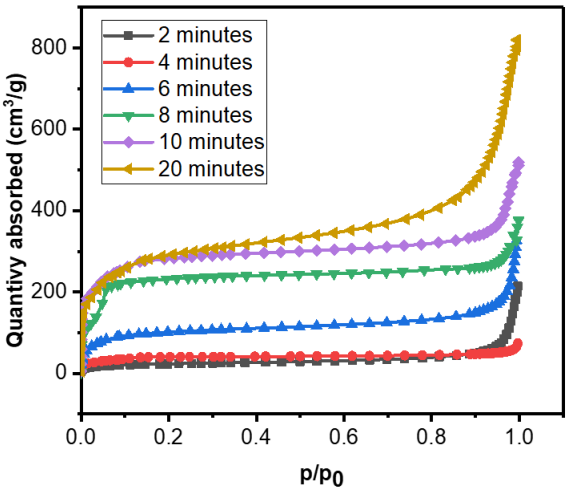

Figure 8. *N_2 gas adsorption isotherm of material at different synthesis times.*

The porous properties of materials synthesized at different times were also surveyed by the N_2 gas adsorption isotherm (figure 8). The results of the calculation of the 2 minutes synthetic, surface area of the material is very small (81.6 m^2/g), this is due to the time of material synthesis to create the frame structure of the material not completed, making the porous properties of the material still low.

When increasing the synthesis time, the frame structure of the material is more complete, so it has an increased surface area, porous properties are achieved at a high level and gradually reach stability when the synthesis time is over 8 minutes (the surface area according to BET is from 887 m^2/g to 1033 m^2/g). With such high porous properties, the material samples have great potential for adsorption. Thus, through the survey process, it is possible to choose the optimal synthesis conditions for MIL-100 (Fe) material both for a high surface area and to ensure the energy-saving factor of 10 minutes.

4. CONCLUSIONS

Metal-Organic Framework materials (MOFs) based on iron (III) and 1,3,5 benzentricacboxylic acid were successfully synthesized by the sonochemical method at various reaction conditions. Through the survey of various factors affecting the synthesis of materials, it has been established the technological process of fabricating Metal - Organic Framework materials by the sonochemical method using 1, 3, 5 - benzentricacboxylic acid (H3BTC) which is organic ligands at reaction conditions: 1080 W power, 10 minutes synthesis time, the ratio of reaction substances of $FeCl_3.6H_2O$: H_3BTC=3:2 with a concentration of ion Fe^{3+} is 0.1 M and the reaction yield reached over 72%. The material obtained has a surface area was relativity high reaching 1033.8 m^2/g, the volume of pores reaching 0.79 cm^3/g. With the application of sonochemical method in the synthesis of MIL-100(Fe) materials, the reaction yield is higher and the reaction time is greatly shortened compared to conventional methods, showing the potential for material fabrication at a larger scale, increasing the practical application of the material.

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TÓM TẮT

Nghiên cứu một số yếu tố ảnh hưởng đến quá trình tổng hợp vật liệu MIL-100(Fe) bằng phương pháp siêu âm

Vật liệu khung cơ kim MIL-100(Fe) đã được tổng hợp thành công trên cơ sở sắt (III) với một phối tử hữu cơ 1,3,5 benzentricacboxylic (H_3BTC) bằng phương pháp siêu âm sử dụng dung môi là nước. Các yếu tố có ảnh hưởng đến quá trình tổng hợp vật liệu đã được khảo sát bao gồm: công suất siêu âm, thời gian phản ứng, tỉ lệ phản ứng, nồng độ chất phản ứng. Kết quả khảo sát cho thấy, điều kiện phù hợp để tổng hợp vật liệu MIL-100(Fe) bằng phương pháp siêu âm là tỉ lệ phản ứng Fe^{3+}:H_3BTC=3:2 với công suất siêu âm 1080 W ở nồng độ 0,1 M trong thời gian 10 phút cho hiệu suất phản ứng đạt hơn 72%. Vật liệu thu được đã được phân tích nhiễu xạ tia X, và đo diện tích bề mặt theo BET. Vật liệu tổng hợp được có diện tích bề mặt cao lên tới 1033,8 m^2/g, thể tích lỗ xốp đạt 0,79 cm^3/g.

Từ khóa: MIL-100(Fe); Phương pháp siêu âm; Hiệu suất phản ứng.